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THE APPLICATION OF CHROMIUM PLATING TO PRINTING
PLATES

I - Introduction¹

¹The essential facts regarding this process were presented at the meeting of the American Electroplaters Society on June 30, 1925. A more detailed article by H. E. Haring, on this subject was published in Chemical & Metallurgical Engineering for August, 1925.

Several years ago the Bureau of Standards in cooperation with the Bureau of Engraving and Printing, developed an electrolytic process for the reproduction of engraved or "in-taglio" plates, such as are used for printing currency and securities. The plates produced by this process, which has been in successful use since that time, have a nickel printing surface, backed up by successive layers of copper and nickel.

In plate printing, the metal surface is rubbed with coarse cloth before each impression to remove the ink from the plane surface and to leave ink only in the engraved lines. This process involves severe abrasion, and hence the nickel plates do not last as long as the case-hardened steel plates, which had been formerly used exclusively. In order to increase the hardness of the surface of the electrolytic plates, the appli-

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cation of chromium plating was considered, because chromium is the hardest metal known.

A process was developed by which about 0.0002" of chromium is deposited upon the nickel surface of an otherwise finished electrolytic plate. The results with about 1000 such plates show that the impressions are even better than from the originals, and that they yield several times as many impressions as the nickel faced or the case-hardened steel plates. It is also possible to deposit the chromium on steel plates which have not been case-hardened and to secure from them greater service than from case-hardened plates. It is too early to estimate the average probable life of the chromium faced plates, but from present indications their use will ultimately result in an annual saving of thousands of dollars to the Bureau of Engraving and Printing.

These results indicate the possible value of chromium plating for other purposes, especially where extreme hardness is required. In some cases it may replace the more troublesome and more expensive case hardening process. Other properties of chromium plating which may prove useful are its high luster and reflecting power and its resistance to tarnish and oxidation and also toward certain chemical reagents.

The investigation of chromium plating at the Bureau of Standards is still in progress. This paper will therefore be confined to certain general principles, and to the actual method used on printing plates. Some modifications of these conditions may be required for other specific purposes.

II - General Principles

Almost all the solutions for chromium plating suggested in recent years have as their principal constituent, chromic acid, CrO_3 ; together with a small amount of chromium sulphate $\text{Cr}_2(\text{SO}_4)_3$, either added as such, or formed in the solution by some means. Experience with solutions containing only these two substances, indicates that erratic results are often obtained. The study conducted at the Bureau has led to the conclusion that in order to produce satisfactory deposits of chromium, it is necessary to maintain the degree of acidity or hydrogen ion concentration within definite limits. It has not been found possible by existing methods to measure the acidity (pH) of these strong solutions of chromic acid. It is possible, however, to regulate the acidity, and keep it within the desired limits by having present in suspension some substance which will be readily formed or dissolved if the acidity changes, i.e. will exert a buffer action.

Such a substance is "chromium chromate", a compound of chromic acid and chromium in the next lower state of oxidation. The chromium chromate may be added as such to the bath, or may be formed in the bath by the addition of any suitable basic or reducing substance, or by the use of chromium anodes, or of lead anodes under proper conditions. It is almost certain that every chromic acid bath thus far proposed contained some of this suspended colloidal chromium chromate when satisfactory deposits were produced even though no steps had been taken to form it intentionally.

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In the actual process at the Bureau of Engraving and Printing, chromium carbonate is added to the solution. This dissolves with effervescence, and forms chromium chromate, the presence of which is indicated by a nearly opaque reddish brown color in place of the ordinary deep orange of chromic acid.

With a given solution and acidity, the cathode efficiency and the character of the deposit depend upon the temperature and current density. Three distinct types of chromium deposit may be produced. At a given current density, by increasing the temperature, we obtain (1) a dull frosty or "burnt" deposit, which may range in color from nearly black to light gray; (2) a brilliant, smooth deposit of as high a luster as the base metal, even after hours of deposition, and (3) a smooth, but scant deposit with a bluish milky appearance. If the temperature is fixed and the current density increased, we obtain in order, the milky, the bright and the burnt deposit.

In Fig. 1, the curves show the relation between cathode efficiency and temperature for several current densities, and the dotted lines indicate the regions within which the three types of deposit are produced. Curve A is for 50 amp./sq.ft., B is 100 amp./sq.ft. and C is 200 amp./sq.ft., on most metals including nickel plated surfaces. Region 1 gives burnt deposits; 2, bright deposits; and 3, scant deposits. It was found, however, that in order to deposit satisfactorily on the nickel face of an electrolytic plate,

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i.e. upon the layer of nickel first deposited in the previous electroforming process, it requires a higher current density than on other surfaces, e.g. 200 amp./sq.ft. instead of 100 amp./sq.ft. It is probable that this difference is due to the effect of the very fine structure of the initial nickel layer. Curve B represents the conditions with 200 amp./sq.ft. upon such a nickel face, and also 100 amp./sq.ft. on other metal surfaces.

From the curves in Fig. 1, it is evident that the metal cathode efficiency is always low, and changes greatly with current density, as does also the character of the deposit. In consequence it is difficult to plate chromium on irregularly shaped articles. In the recessed parts there is likely to be little or no deposit, while on exposed parts the deposit may be gray or burnt. The extreme hardness of chromium makes it difficult to produce, by buffing or polishing, a high luster on a dull chromium surface. Extensive application of chromium plating will therefore depend upon a marked improvement in throwing power.

In plating chromium especially upon iron or nickel, it is necessary to have the current on the cathode when it is introduced into the bath. If this is not done, the surface becomes "passive", and those parts which would normally receive a low current density, will receive no deposit. Hence the apparent throwing power will be even worse than under the favorable conditions.

It is possible to strip chromium from steel or nickel by a

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reverse current in chromic acid, which does not attack these metals. To remove chromium from copper or brass it may be made the anode in dilute hydrochloric acid, or may be treated directly without a current with (1 - 3) hydrochloric acid.

III - Operating Conditions

The solution used at the Bureau of Engraving and Printing is prepared from:

	g/L	oz/gal
Chromic acid CrO_3	250	33
Chromium sulphate $\text{Cr}_2(\text{SO}_4)_3$	3	0.4
Chromium carbonate $\text{Cr}_2\text{O}(\text{CO}_3)_2$	7	1.0

The exact concentrations are not however important. The composition may be controlled by chemical analysis, in which the chromium present in the three forms is indirectly determined.

The solution is contained in a stoneware jar, which is immersed in water in a larger tank. The anodes consist of sections of lead pipe with a total area equal to about one-half that of the cathode surface to be plated, and so placed as to produce a nearly uniform current density on the cathode. Behind the latter (which is plated on only one side), a coil of lead pipe is suspended, through which hot or cold water can be circulated to regulate the bath temperature. Very good ventilation is required, as a large amount of spray is formed, which is injurious to the nasal septum.

The plates are cleaned as cathodes in an alkaline cleaner, scrubbed with pumice, rinsed in warm water, rapidly dried, and placed in the bath in such a way as to complete the circuit. Drying is advantageous, but not absolutely necessary.

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The bath is kept between 104 and 122°F (40° and 50°C) and preferably at 113°F (45°C). On steel plates the current density is 100 amp./sq.ft. (11 amp./dm²) which requires about 7 volts, and on electrolytic plates, 200 amp./sq.ft. (22 amp./dm²) using 9 volts. In both cases the metal cathode efficiency is about 12 per cent. In order to deposit about 0.0002" (0.005 mm) of chromium, the steel is plated for sixty minutes and the electrolytic nickel for thirty minutes.

CATHODE EFFICIENCY % $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}$



